

[Reprinted from AMERICAN CHEMICAL JOURNAL, Vol. X, No. 6.]

ON THE OCCURRENCE OF ARSENIC IN GLASS AND  
IN THE CAUSTIC ALKALIES,

WITH AN EXAMINATION OF THE ACTION OF THE STRONG ACIDS,  
CAUSTIC ALKALIES, AND OTHER REAGENTS, UPON  
ARSENICAL GLASS.

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Over forty years ago the Academy of Medicine of Paris, at the request of the French Government, undertook the investigation of the occurrence of arsenic in glass, and as a result of the research declared that "the glass which they examined contained no arsenic, and although arsenic is sometimes used in glassmaking, and a trace of it may be retained in some opaque glasses or enamels, it cannot be detected by any process of analysis in any of the clear glass met with in commerce, *all of the arsenic being volatilised* during the manufacture of the glass."<sup>1</sup>

It is well known that arsenious oxide is extensively used in the manufacture of glass, principally to decompose the sodium sulphide formed in the process,<sup>2</sup> and also to effect the removal of color from the glass mixture containing carbon or silicate of iron. The arsenious oxide is reduced to the metallic form by the carbon and ferrous oxide at a dull red heat, and according to Wagner<sup>3</sup> and others, the *arsenic is volatilised*. Further on, however, Wagner (p. 392) states that in the use of arsenic in glassmaking, it should not be overlooked that a small portion of the arsenic remains in the finished glass as calcium arsenite or arseniate.

For some years past the presence of traces of arsenic in glass has been admitted. Lately, W. Fresenius<sup>4</sup> has determined it to be present in considerable quantity in some samples of Bohemian glass tubing, such as is used in many laboratory operations. In one of the three samples he found as much as 0.2 per cent. of arsenic. Again, M. Kreusler<sup>5</sup> found in a sample of Thuringian

<sup>1</sup> Annales d'Hyg. Pub. et de Med. 11, 224.

<sup>2</sup> Post. Chemische Technologie 2, 17.

<sup>3</sup> Handbuch d. chem. Tech. 1886, 392.

<sup>4</sup> Ztschr. anal. Chem. 22, 397.

<sup>5</sup> Wagner, Handbuch d. chem. Tech. 1886, 386.



glass 0.15 per cent. of  $\text{As}_2\text{O}_5$ . In a sample of Bohemian combustion tubing the same investigator found 0.12 per cent. of  $\text{As}_2\text{O}_5$ , and in an easily fusible potash glass 0.10 per cent. of  $\text{As}_2\text{O}_5$ . The finding of arsenic in such quantity disproves the old belief that *all the arsenic is volatilised*. Upon inquiry at a glass bottle manufactory in Philadelphia, it was learned that in the process employed in the establishment, approximately twenty pounds of arsenious oxide were used to each melting of four thousand pounds of glass, and in making clear glass the pots were kept closed with a lid, thus in a measure preventing the escape of any arsenic that might volatilise.

The following investigation was begun primarily to determine the presence of arsenic in glass of American manufacture, but its scope was somewhat enlarged and glass of foreign make was included. The action of the caustic alkalies, strong acids, and ordinary laboratory reagents, upon the arsenical glass of the bottles in which they were contained, was also studied. The occurrence of arsenic in commercial caustic soda, sodium carbonate, and also in sodium hydrate and sodium carbonate sold as chemically pure, was investigated. In every case the presence of arsenic was first determined qualitatively by Marsh's test, and when found, a quantitative determination followed. In examining the glass for arsenic the following method was employed: The glass was pulverised in an agate mortar, then mixed with sodium carbonate, and fused. The fused mass was broken up and dissolved in water, then acidified with sulphuric acid, the separated silica filtered off, and the filtrate placed in the Marsh apparatus.

The reagents employed, sodium carbonate, sulphuric acid, and zinc, were tested in long continued control experiments and found to be perfectly free from arsenic. Lead was found in some of the samples of glass, but no quantitative determinations were made.

In the quantitative estimations the glass was pulverised as before and fused with sodium carbonate. The fused mass was broken up, dissolved in water, and acidified with sulphuric acid. The silica was filtered off, and the filtrate, to which had been added a solution of sulphurous acid gas, was evaporated to a small volume on a water-bath, and then diluted with a little hot water and filtered from the remaining separated silica. Through the warm filtrate a washed stream of hydrogen sulphide was passed for several hours, and the precipitated arsenious sulphide collected on a filter paper



and washed. The precipitate was then dissolved, while on the filter, with a few drops of dilute ammonium hydrate, the solution evaporated to dryness, and the residue warmed with strong nitric acid until the sulphide was completely oxidised. The acid was driven off by evaporation to dryness, and the residue was warmed with a little water and then filtered. Magnesium mixture was added to the filtrate and the whole allowed to stand twenty-four hours. The precipitated magnesium ammonium arseniate was collected on a filter paper and the arsenic weighed as magnesium pyro-arsenate.

	Quantity of glass employed.	Description.	Where made.	Amount of $Mg_2As_2O_7$ obtained.	Equivalent percentage of $As_2O_3$ .
I	5.0 grams	8-liter bottle	Germany	0.010	0.127
II	5.0 "	Reagent bottle	Philadelphia	0.015	0.191
III	5.0 "	Beaker	"	0.024	0.306
IV	2.0 "	Reagent bottle	"	0.008	0.255
V	2.0 "	Refractory tubing	Thuringia	0.003	0.095
VI	5.0 "	8-liter bottle	Germany	0.008	0.102
VII	5.0 "	Beaker	Philadelphia	0.035	0.446

When glass tubing No. 5, which contained arsenic, but no lead, was used as a reduction tube and pure hydrogen passed through in Marsh's test, the brown coloration referred to by Fresenius<sup>1</sup> as produced directly at the point in contact with the flame invariably appeared.

*Examination of the Caustic Alkalies, the Strong Acids and other Reagents, for the Presence of Arsenic, and Investigation of their Solvent Action upon the Arsenical Glass of the Bottles in which they were contained.*

In testing the alkalies, sulphuric acid was used for acidifying. The strong acids were sufficiently diluted with distilled water, or partly neutralised with sodium carbonate before testing.

In all but one of the samples of caustic soda examined, arsenic was found, varying from a trace to quite a considerable percentage. Four samples of caustic potash were examined, but no arsenic was detected.

*Qualitative.*

I. Two samples, each containing twenty grams of sodium carbonate, sold as chemically pure and obtained from different

<sup>1</sup> Ztschr. anal. Chem. 22, 400.

German makers, separately neutralised with sulphuric acid and tested in Marsh's apparatus, gave different results. One sample furnished a very slight mirror, the other gave no indication of the presence of arsenic.

II. Ten grams of sodium hydrate, in sticks made in Philadelphia, gave a slight mirror. These sticks were contained in an arsenical glass bottle, so that care was taken to select the sticks not in direct contact with the glass. The end in contact with the bottom or side of the bottle was broken off and rejected.

III. Ten grams of caustic soda, made by the Solvay process, failed to show the presence of arsenic.

### *Quantitative.*

In estimating the quantity of arsenic in the alkalies, they were dissolved in water, then rendered slightly acid with sulphuric acid, sulphurous acid added, and the latter driven off by heating the liquid. Hydrogen sulphide was passed through the solution, the precipitated arsenious sulphide was collected on a filter, washed, dissolved in ammonium hydroxide, the solution evaporated to dryness, and the residue of arsenious sulphide oxidised with nitric acid. The nitric acid was driven off by heat, the residue dissolved in water, filtered, magnesium mixture added to the filtrate, the precipitate was collected on a filter, and the arsenic weighed as pyro-arsenate.

I. One hundred grams of sodium hydrate in sticks, made by a Philadelphia firm, furnished 0.0044 gram of  $Mg_2As_2O_7$ , equivalent to 0.0028 per cent. of  $As_2O_3$ .

II. Three grams of a very white caustic soda, sold as chemically pure, gave 0.004 gram of  $Mg_2As_2O_7$ , equivalent to 0.0848 per cent. of  $As_2O_3$ .

III. Ten grams of another sample of white caustic soda, represented to be chemically pure, yielded 0.0062 gram of  $Mg_2As_2O_7$ , equivalent to 0.039 per cent. of  $As_2O_3$ .

IV. Twenty grams of a sample of "crude carbonated soda," made in England, furnished 0.021 gram of  $Mg_2As_2O_7$ , equivalent to 0.067 per cent. of  $As_2O_3$ .

In order to study the solvent action of caustic soda upon glass, bottles of arsenical glass of about 500 cc. capacity were filled with a 10 per cent. solution of sodium hydroxide (free from arsenic) and allowed to stand different periods of time.



I. 20 cc. of the solution which had been allowed to stand in a bottle five months, when tested with Marsh's test, produced a very strong mirror in six minutes.

II. 20 cc. of the solution contained in a bottle one month gave a decided mirror in ten minutes.

III. 20 cc. of the solution which had been kept in a bottle twenty-three hours gave no reaction. Twenty cubic centimetres of this solution were tested after the lapse of every twenty-three hours, and no arsenical mirror appeared until the sixty-ninth hour.

IV. 20 cc. of a 10 per cent. solution of potassium hydroxide kept in a bottle twenty-four hours readily produced an arsenical mirror.

The strong acids, sulphuric and hydrochloric, which were examined had been kept in large (eight-liter) arsenical glass bottles for different lengths of time. The bottles being of large size, quite an extensive surface of glass was exposed to the action of the acid. The acids, previously neutralised with sodium carbonate (free from arsenic), were tested in Marsh's apparatus.

I. 40 cc. of strong hydrochloric acid (American), kept in an arsenical glass bottle three months, gave no trace of arsenic.

II. 40 cc. of strong hydrochloric acid (German), contained in an arsenical glass bottle three years, failed to give a trace of arsenic. The glass of the bottle in which this acid was kept contained 0.102 per cent. of  $\text{As}_2\text{O}_3$ .

III. 40 cc. of strong sulphuric acid (American), contained in an arsenical glass bottle three months, did not give a trace of arsenic.

IV. 40 cc. strong sulphuric acid (German), contained in an arsenical glass bottle six years, failed to give any indication of arsenic. The glass of this bottle contained 0.127 per cent. of  $\text{As}_2\text{O}_3$ .

Some of the ordinary laboratory reagents kept in arsenical glass bottles were tested with Marsh's test, but, as shown below, failed to give any indication of the presence of arsenic.

Two samples, 50 cc. each, of ammonium hydroxide, kept respectively one and two months, failed to show arsenic. Solutions of potassium nitrate and chlorate and a strong solution of barium chloride kept in arsenical glass bottles, failed to produce a mirror.

Sodium carbonate, which originally contained arsenic, was after several recrystallisations found to be entirely free from the metal.

It will be observed that every sample of clear glass examined except one, and all the caustic soda except one sample (that made by the Solvay process), contained arsenic. The caustic potash,

ammonium hydroxide, and the common reagents examined were found to be free from arsenic. The strong acids, ammonium hydroxide, and ordinary reagents had no dissolving action upon the surface of arsenical glass bottles, whereas solutions of the fixed alkalies had such solvent action.

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